The Adsorption Heat of the Vapors of Benzene and Hexane on Quartz

20-119-4-28/60

a condensed powder there were interspaces with mostly 1000 to 7000 Å. With an increase of p/p_s from the beginning of hysteresis to saturation about 70% of the surface disappear. A further diagram, by way of comparison, illustrates the isothermal lines of the adsorption of the same vapors on a homogeneous silica gel KSK-2. The desorption branch begins to decline steeply near $p/p_s = 0.7$. In this domain the adsorption on quartz is not yet rendered complicated by any capillary condensation in the interspaces between the particles. In the initial domain of monomolecular filling-up adsorption on quartz is greater than on silica gel KSK-2, which is connected with the lower skeleton density of this silica gel. Further details are given. A further diagram shows the dependence of the heat of adsorption of benzene vapors upon the absolute value α of the adsorption on quartz. After filling-off of the first two layers adsorption heat exceeds condensation heat only by 3%, and after the adsorption of 4 layers by 1%. Further reduction of the heat of adsorption takes place very slowly. The

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... on quartz. Also in this case a gradual decrease of adsorption heat is observed. The authors then mention some numerical data dealing with this subject. There are 4 figures and 18 references, 13 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy univers[illegible] (Moscow State University imeni M.V. Lomonosov)

PRESENTED: August 10, 1957, by M. M. Dubinin, Member, Academy of Sciences, USSR

SUBMITTED: June 27, 1957

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SOV/20-120-4-40/67

AUTHORS: Kiselev, A. V., Poshkus, D. P.

TITLE: The Energy of the Coulomb Interaction Between the Hydroxyl Group of Silica Gel and the Benzene Molecule (Energiya kulonovskogo vzaimodeystviya gidroksil'noy gruppy silikagelya s molekuloy benzola)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 834 - 837 (USSR)

ABSTRACT: In the computations discussed in this paper the hydroxyl group is considered to be a system of two point charges the position of which agrees approximately with the position of the oxygen atom and of the hydrogen atom. A formula is written down for the energy of the Coulomb (Kulon) interaction between the hydroxyl group and the benzene molecule; this energy was computed for various subcases in a vertical position of the hydroxyl group with regard to the direction of the benzene ring. The same energy in the case of a displacement of the hydroxyl group inside the benzene ring depends only in a low degree on their mutual position and amounts to about 4-6 kcal/mol. This interaction energy decreases considerably outside the benzene

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ring. According to the data obtained, the energy of the Coulomb interaction between the polar hydroxyl group and the non-polar benzene molecule is high and in the formation of the hydrogen binding in a given system it plays the decisive role among the other interactions. The benzene molecule adsorbed on the surface of a completely hydrated silica gel interacts essentially with one or with only a few hydroxyl groups; besides, such an adsorbed benzene molecule also interacts with the other atoms of the lattice of the silica gel. Therefore the removal of the hydroxyl groups from the surface of the silica gel is bound to decrease the heat of adsorption of the benzene molecules on the dehydrated surface of the silica gel. Besides, the energy of the interaction of the adsorbed benzene molecule must be increased with the volume phase. The computed energy of the Coulomb interaction (about 4-6 kcal/mol) agrees satisfactorily with the experimental values of the decrease of the adsorption heat of benzene in the dehydratization of the surface of silica gel. There are 1 figure and 2o references, 7 of which are Soviet.

The Energy of the Coulomb Interaction Between the Hydroxyl Group of Silica Gel and the Benzene Molecule

SOV/20-120-4-40/67

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im.M.V.Lomonosova (Moscow State University imeni M.V.Lomonosov) Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry AS USSR)

PRESENTED: January 18, 1958, by A.N.Frumkin, Member, Academy of Sciences, USSR

SUBMITTED: January 18, 1958

1. Hydroxyl radicals--Chemical reactions 2. Benzenes--Chemical reactions 3. Benzene molecules--Adsorption 4. Silicon dioxide--Chemical properties 5. Chemical reactions--Energy

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5(4) SOV/62-59-2-7/40

AUTHORS: Kiselev, A. V., Neymark, I. Ye., Poshkus, D. P., Piontkovskaya, M. A.

TITLE: Change of Porous Structure of Magnesium Hydroxide During Heat Treatment (Izmeneniye poristoy struktury gidrookisi magniya pri termicheskoy obrabotke)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 2, pp 232-237 (USSR)

ABSTRACT: In the present paper the change of the porous structure of magnesium hydroxide during heat treatment in the vacuum was investigated in a broad temperature range. It was found that the magnesium hydroxide pumped off at 200° represents a broad-porous sample (d=450 Å) with large pore volume (v_s = 0.71 cm³/g). The values of the specific surfaces of the skeleton and of the adsorption layer s are approaching one another in the initial sample. This indicates that therein micropores are occurring to practically no extent, which are filled up in the primary adsorption process without hysteresis. On the transition of this hydroxide into oxide the specific surface is considerably increased at 350° (by

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about the 3-fold). Volume and size of the pores in which capillary condensation takes place remain, however, unchanged. The formation of the micro-structure is due to water separation from the hydroxide lamellae and to the transformation of the crystal structure of $Mg(OH)_2$ into MgO structure at which the molar volumes are different. At 350° the sample is of bi-disperse structure; it keeps the homogeneous coarsely porous structure of the initial substance but the walls of this structure are traversed by fine pores (cracks). A further increase of the calcination temperature up to 500° causes already a certain agglomeration of the micro-structure, as the specific surface becomes smaller. On a further increase in temperature up to 1000 and 1400° also the large pores are considerably contracted. In consequence of this not only the size but also the surface of the adsorption layer s' and the volume of the pores ν_s decrease. In samples obtained at 1400° the size of the specific surface s is getting nearly as large as the size of the adsorption layer s'. This means that in this sample the fine pores disappear and the structure

Change of Porous Structure of Magnesium Hydroxide During Heat Treatment SOV/62-59-2-7/40

passes over again from a bi-disperse (fine and coarsely porous) into a homogeneous coarsely porous one. There are 3 figures, 1 table, and 23 references, 12 of which are Soviet.

ASSOCIATION: Instituty fizicheskoy khimii Akademiy nauk SSSR i USSR (Institutes of Physical Chemistry of the Academies of Sciences, USSR and UkrSSR) Moskovskiy gosudarstvennyy universitet im M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: July 1, 1957

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5(4)

SOV/62-59-3-5/37

AUTHORS: Kiselev, A. V., Lygin, V. I.

TITLE: Electron-microscopic Study of Porous Structure of Magnesium Hydroxide and Its Changes Associated With Thermal Treatment (Elektronno-mikroskopicheskoye issledovaniye poristoy struktury gidrookisi magniya i yeye izmeneniy pri termicheskoy obrabotke)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 412-416 (USSR)

ABSTRACT: In the present paper the macroporous structure of magnesium-hydroxide samples and products of their thermal decomposition was investigated by means of carbon copies. As investigation objects the homogeneously wide-porous magnesium-hydroxide samples calcined at 200° and the magnesium-oxide samples obtained from them by means of calcination at 1,000 and 1,400° were used. The recordings of the carbon copies and samples against light were taken in the electron microscope UEM-100 at a voltage of 60 kv. The skeleton of magnesium hydroxide has a corpuscular structure and consists of laminar crystallites (Figs 2,3). Some of these crystallites have a strongly hexagonal and some a distorted form. On the

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Electron-microscopic Study of Porous Structure of Magnesium Hydroxide and Its Changes Associated With Thermal Treatment

stereo-microphotography (Fig 6) carbon copies of samples which were calcined in vacuum at 1,000° are shown. The data obtained by electron-microscopic investigation as well as the determination results obtained by the adsorption method (Ref 13) are given in the table. It was found that the calcination of the initial samples in vacuum at 1,000° is followed by a condensation of the original structure (the diameters of the pores decrease down to 300-350 Å). The laminar form, however, is maintained. This indicates that the changes observed in adsorption measurements (Refs 13,15) of the specific surface during calcination in the temperature range of 200-1,000° are mainly connected with the transformation of the structure within the hydroxide lamellae. The form of the lamellae and wide-porous skeleton formed by them does not vary considerably. Thus the electron-microscopic investigation confirms the conclusion drawn from the adsorption measurements (Ref 13) regarding the formation and disappearance of the bidisperse structure in the course of thermal treatment. Quite a different character is exhibited by the hydroxide sample calcined at 1,400° (Fig 4). The stereo-microphotograph

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Electron-microscopic Study of Porous Structure of Magnesium Hydroxide and Its Changes Associated With Thermal Treatment SOV/62-59-3-5/37

shows an extremely porous cut and the lamellae do not appear any longer. This is apparently a consequence of the agglomeration of some lamellae taking place at this temperature and of the considerable growth of crystallites within the lamellae. At the same time the general character of the macroporous structure is maintained also at these calcination temperatures. This is likewise in accordance with the determination results obtained by the adsorption method. There are 7 figures, 1 table, and 16 references, 13 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov) Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: July 8, 1957

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5(4) SOV/62-59-5-5/40

AUTHORS: Avgul', N. N., Berezin, G. I., Kiselev, A. V., Lygina, I. A.

TITLE: Adsorption Heat of a Number of Isoalkanes, Naphthenes and of Toluene on Graphitized Carbon Black (Teplota adsorptsii ryada izoalkanov, naftenov i toluola na grafitirovannoy sazhe)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 787 - 796 (USSR)

ABSTRACT: In this work the following hydrocarbons were investigated as to their adsorption heat: three isoalkanes (neohexane, isoheptane, and isooctane), two alicyclic hydrocarbons; cyclopentane and methylcyclopentane, and the alkylaromatic compound toluene. The hydrocarbons had been selected in this way in order to investigate the effect of the chain branching, the ring formation of these chains, and the introduction of aliphatic substituents into the naphthene and benzene ring on adsorption. The hydrocarbons used in the investigations had been synthetized at the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry of the AS, USSR) by Ye. A. Mikhaylova, A. F. Plate, A. L. Liberman, and S. V. Zotova. The authors express their gratitude for their help. The constants of these substances are summariz-

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Adsorption Heat of a Number of Isoalkanes, Naphthenes SOV/62-59-5-5/40
and of Toluene on Graphitized Carbon Black

ed in table 1. "Sferon"-6 was used as adsorbent; it was graphitized at 1700°. The differential adsorption heat was determined at 20° in a calorimeter with constant heat exchange; the amount of the adsorption was determined by means of a capillary vacuum liquid microburet. Figures 1, 2 show the isothermal lines of adsorption of the various substances and figures 3, 4 show the dependence of the differential adsorption heat on the amount of heat adsorbed by the individual substances. The figures show that the normal adsorption heat of isoalkanes and naphthenes is lower than that of the corresponding n-alkanes. The value of the adsorption heat of cyclopentane amounts to only half of that of n-pentane. Cyclopentane, therefore, shows greater attraction towards the adsorption layer, its isothermal line of adsorption is concave at its beginning. It can be seen from the thermodynamic evaluation of the experimental data obtained that the isothermal line of adsorption of cyclopentane cannot be represented by the Langmuir equation or BET equation but by an equation which allows for the interaction adsorbate-adsorbate

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Adsorption Heat of a Number of Isoalkanes, Naphthenes and of Toluene on Graphitized Carbon Black SOV/62-59-5-5/40

(Fig 5). The entropy curves (Fig 6) indicate that the state of isoalkanes and naphthenes in the dense adsorption layer on graphite is much closer to the liquid state than that of n-alkanes. The methyl group in the toluene molecule reduces its mobility with respect to the unsubstituted benzene and the other purely cyclic compounds. With regard to the theoretical calculation of adsorption heat it was assumed that, in the case of the ramified hydrocarbons, the adsorption heat is an additive function of the number of carbon atoms in the molecule. The free adsorption energy and the surface of the adsorbent occupied by molecules were determined according to the same assumption. There are 6 figures, 3 tables, and 17 references, 12 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: July 25, 1957

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5 (4) SOV/62-59-6-6/36

AUTHORS: Kiselev, A. V., Kovaleva, N. V.

TITLE: The Influence Exercised by the Thermal Treatment of Different Carbon Blacks Upon the Adsorption of Vapours (Vliyaniye termicheskoy obrabotki razlichnykh sazh na adsorbtsiyu parov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 989-998 (USSR)

ABSTRACT: As is well known, an increase in treatment temperature causes an increase in the crystal dimension up to parallel orientation, as is the case with the graphite lattice. Besides, there are numerous papers which deal with the investigation mentioned in the title (Refs 1-40). It is only the problem of the fundamental adsorption changes of different substances that has scarcely been dealt with up to now. As to this problem there are different opinions as to whether the presence of oxygen complexes on the surface of the adsorbents, or the inhomogeneity of the surface are to be made responsible for the adsorption. In this connection, the adsorption was investigated in the present work as being dependent on the surface quality (roughly inhomogeneous, strongly, and weekly oxidized carbon black). Subject to investigation were substances with extreme structure and polarity

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such as benzene, water, methanol. For this purpose the adsorption isotherms of the above mentioned substances on carbon black adsorbents (Figs 1-6) submitted to different thermal treatment were determined. It was found that with increasing treatment temperature, the quantity of oxygen needed for the exchange with NaOH in aqueous solution on the surface of the carbon black decreases, and so does the roughness of the surface. It remains homogeneous after treatment in hydrogen at 1700°. The steam adsorption by graphite treated carbon black which also decreases is mainly due to the elimination of surface oxides. With graphite treated carbon black in a hydrogen current adsorption of water is very low, even at high pressure. The adsorption of methanol vapours also decreases by the elimination of the surface oxides, while the decrease in the surface roughness here only plays an unimportant rôle. Benzene adsorption with graphite treatment is mainly reduced because of the adsorbent surface which is not rough enough. In general graphite treatment in hydrogen current at 1700° of different types of carbon black leads to quite similar surface qualities of the adsorbent. The authors thank M. M. Dubinin for explanations he gave them.

The Influence Exercised by the Thermal Treatment of Different Carbon Blacks Upon the Adsorption of Vapours SOV/62-59-6-6/36

There are 6 figures, 2 tables, and 45 references, 16 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: November 11, 1957

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5 (2), 5 (4) SOV/62-59-7-7/38

AUTHORS: Avgul' N. N., Kiselev, A. V., Lygina, I. A., Poshkus, D. P.

TITLE: A Contribution to the Calculation of the Energy of the Adsorption of Nonpolar Molecules on Graphite (K raschetu energii adsorbtsii nepolyarnykh molekul na grafite)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1196-1206 (USSR)

ABSTRACT: In this paper the details of a calculation of the adsorption energies of simple and compound molecules carried out in a previous paper are represented. The calculations were carried out according to the formulas from paper reference 1 according to which the adsorption energy is determined by the expressions

$$\Phi_i' = -C_{i1}\sum_j r_{ij}^{-6} - C_{i2}\sum_j r_{ij}^{-8} - C_{i3}\sum_j r_{ij}^{-10} + B_i'\sum_j e^{-r_{ij}/\varrho}$$

$$\Phi_i'' = -C_{i1}\sum_j r_{ij}^{-6} - C_{i2}\sum_j r_{ij}^{-8} - C_{i3}\sum_j r_{ij}^{-10} + B_i''\sum_j r_{ij}^{-12}$$

r_{ij} is the distance of the center of the i-th adsorption molecule from the center of the j-th atom of the adsorbent.

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A Contribution to the Calculation of the Energy of the Adsorption of Nonpolar Molecules on Graphite SOV/62-59-7-7/38

$C_{i1,2,3}$ are constants of the dispersion reaction, B' and B" are the constant of the exponential function and the constant of the repulsion preceding the powers. ϱ is an exponential constant of the repulsion. The calculation is carried out in two parts, the geometric one in which the distances of the adsorbed link i to all atoms j of the lattice of the adsorbent are calculated for different distances of the former from the surface. For this calculation only the lattice constants of the adsorbent have to be known. For the second part of the calculation of the forces the constants charaterizing the reactions of both substances have to be determined. The calculation of the sums of r_{ij} was carried out for n = 6, 8, 10 and 12 for the different distances of the adsorbed link from the basis of the adsorbent equal to 2, 2.5, 3, 3.5 a (a is the distance of the nearest atom). In table 1 the results of the calculation of the sums $\sum^{r_i} r_{ij}^{-n}$ are combined. The distances of the remaining graphite volume were determined from the integrals (3), (4), (5) (Table 2).

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A Contribution to the Calculation of the Energy of the Adsorption of Nonpolar Molecules on Graphite SOV/62-59-7-7/38

The sums $\sum^{r_i} r_{ij}^{-n} + \int_{(n)}$ are represented in tables 4 and 5 and the graphic representation in figure 2. The value $\sum e^{-r_{ij}/0.28}$ for ϱ in table 6 was equated to 0.28 according to reference 6. For the sums of tables 4, 5 a simplified form with the constants p_n and q_n, the values of which are given in table 7, is introduced and the functions (1) and (2) are represented in the variable z (6), (7). $\left(\sum^{r_i} r_{ij}^{-n} + \int_n = p_n z^{-q_n}\right)$. Next, the calculation of the reaction constant $C_{i1,2,3}$ is carried out. The values for different adsorptives are given in table 7 with the constants α and χ (polarizability, magnetic susceptibility) being necessary for the calculation of $C_{i1,2,3}$. Φ' and Φ'' were then determined by the aid of computed constants. The results for Φ''

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are given in tables 10 and 11. The calculation of the attraction- and repulsion constants was carried out from the balance energy of the adsorption of compound molecules on the basis of an additive scheme. There are 6 figures, 11 tables, and 8 references, 2 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR) Khimicheskiy fakul'tet Moskovskogo gosudarstvennogo universiteta im. M. V. Lomonosova (Chemical Department of the Moscow State University imeni M. V. Lomonosov)

SUBMITTED: November 16, 1957

SOV/76-33-2-23/45

5(4)

AUTHORS: Isirikyan, A. A., Kiselev, A. V., Frolov, B. A.

TITLE: The Heat of Adsorption of Normal Alkanes on Silica Gels (Teplota adsorbtsii normal'nykh alkanov na silikagele)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 2, pp 389 - 394 (USSR)

ABSTRACT: In continuation of the work of previous papers (Refs 10,11, 16 - 19) the heat of adsorption (AH) of n-pentane (I) and n-octane (II) on coarsely porous silica gels was measured. An adsorption calorimetric apparatus was used which is a simplified variant (Ref 20) constructed in cooperation with G. G. Muttik and which will be described separately. As in the other papers (Refs 10,11,13,16) a homogeneously porous silica gel KSK-2 with a specific surface of 320 m^2/g and a pore diameter of about 100 Å was used. A comparison of the obtained absolute adsorption isotherms (Fig 1) for (I) and (II) with those for n-hexane and n-heptane on the same silica gel (Ref 10) shows that the (AH) from pentane to octane increases and it is not possible to apply the BET equation. Since the constant of the induction interaction with the

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electrostatic field is proportional to the polarizability of the n-alkanes the general adsorption energy on the silica gel also increases linearly with the number of carbon atoms in the molecule. The linear functions Q_a^o of n (n= number of carbon atoms)(Fig 3) and the standard differential (ΔH) of the n-alkanes were derived for adsorption on silica gels, carbon black (Refs 4,5), MgO (Ref 7), and water (Ref 27). The values for any particular n-alkane can be calculated from the following equations:

Adsorption on carbon black $Q_a^o = 0.7+1.9$ n kcal/mol (n= number of carbons)

" " MgO $Q_a^o = 0.6+1.5$ n kcal/mol "

" " silica gel KSK-2 $Q_a^o = 1.0+1.3$ n kcal/mol "

Heats of condensation $L = 0.4+1.2$ n kcal/mol

Adsorption on water $Q_{a \to o} = 1.7+0.7$ n kcal/mol. There are 3 figures, 1 table, and 27 references, 24 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: July 17, 1957

5 (4) SOV/76-33-7-14/40

AUTHORS: Belyakova, L. D., Kiselev, A. V.

TITLE: Adsorption and Chemisorption of Methanol by Silica Gels With Different Degrees of Surface Hydration

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 7, pp 1534 - 1543 (USSR)

ABSTRACT: It was already found in previous papers (Refs 1-4) that the adsorption (A) of methanol (I) by silica gel (II) depends largely on the degree of surface hydration, and that chemisorption takes place. In the present paper, the authors investigated a variation in the adsorption and chemisorption properties of coarse-pored silica gels (KSK-2) (with respect to (I)) which was due to great changes in the α_{OH} (α_{OH} = concentration of OH on the silica-gel surface) in the case of small structural changes of the pores. Experiments were made in a vacuum apparatus (Fig 1) consisting of three separate measuring arrangements. The samples were annealed at various temperatures (200 - 1020°). The specific surface s of the sample was determined from the (A) of nitrogen, and on the basis of these data and the content of structure water the authors

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Adsorption and Chemisorption of Methanol by Silica Gels With Different Degrees of Surface Hydration SOV/76-33-7-14/40

calculated the values of α_{OH} (Fig 2). Within the range 200 - 800° α_{OH} falls practically in a linear manner. Heating up to 950° reduces s and v_s (total volume of the pores) only by 20%, while the size of the pores (d≈100 Å) does not vary. Heating up to 1020°C, however, decreases s and v_s by about 75%, and d drops to 55 - 70 Å. A comparison (Table 1) of the quantity of irreversibly chemisorbed (I) α_{OCH_3} with α_{OH} indicates that, contrary to the rapid physical adsorption, α_{OCH_3} increases with decreasing α_{OH}. The primary (A) of (I) from KSK-2 (at 200°) proceeds much faster than on KSK-2 (at 650°) or KSK-2 (at 1020°). Kinetic curves indicate that the chemisorption of (I) on the hydrated surface of (II) differs greatly from that on dehydrated surfaces. Experiments on thermal decomposition of the surface compound of (I) with (II) showed (Table 2) that only

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Adsorption and Chemisorption of Methanol by Silica Gels With Different Degrees of Surface Hydration SOV/76-33-7-14/40

7% of the irreversibly adsorbed substance are removed by heating to 200° approximately. Methoxylation of the (II)-surface reduces the (A) of (I)-vapors, i.e. the reaction of (I) with the OH-groups of the (II)-surface is greater than the one with the OCH_3 groups. The chemisorption of (I) on (II) increases with decreasing concentration of the OH-groups on the (II)-surface. This is due to the surface methoxylation. In this process, a reaction takes place between the OH-group of silicic acid, and the bond Si - O - Si decomposes to form Si-OH and Si-OCH_3-groups. The adsorption of (I), water, and benzene decreases particularly strongly (4 times approximately) within the range $\alpha_{OH} = 7 - 4\ \mu mol/m^2$. In conclusion, the authors thank V. S. Bronshvager and G. G. Muttik for their assistance. There are 8 figures, 2 tables, and 27 references, 24 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: December 30, 1957

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5(4)

AUTHORS: Gryazev, N. N., Kiselev, A. V. SOV/76-33-7-20/40

TITLE: Adsorption Isothermal Lines From Three-component Solutions

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 7, pp 1581-1593 (USSR)

ABSTRACT: The development of adsorption chromatography of multi-component mixtures requires investigation of the adsorption equilibrium, i.e. of the adsorption isothermal lines (AI) of the components of such mixtures. The (AI) of the following liquid three-component solutions were investigated in this case: cetane (I) + acetic acid (II) + lauric acid (III), (I) + (II) + palmitic acid (IV) and (I) + (II) + α-methyl naphthalene (V). The authors chose these mixtures because (I) and (IV) serve the purpose of modeling the adsorptive regeneration of mineral oils; on the other hand, (II) is soluble in (I) to a certain extent, while (III) and (IV) are perfectly soluble in (I), and because the influence exercised by a variation of the solubility of the three-component solutions upon their adsorption can be investigated. One of the most active sedimentation rocks with a

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high silica content, called "opok" (Nr 120 from the area round the village of Kamennyy Yar, Stalingrad oblast') and an industrial KSK-4 silica gel were used as adsorbents. The characteristic values of the mixture components applied are given. Adsorption experiments were made by a method devised by the Laboratoriya adsorbtsii Moskovskogo universiteta (Laboratory for Adsorption of Moscow University)(Ref 15). An ITR-2 interferometer and an IRF-22 refractometer were used for analyzing the binary systems. The method of analysis of the three-component solutions and the evaluation of the results obtained are described. Three-dimensional diagrams illustrate the resultant (AI). The authors found that additions of the third component to the binary mixture decrease the adsorption of the components and change the course of the (AI). A change in the solubility of the components from limited into unlimited solubility effects a variation of the S-shaped isothermal lines into lines with a

Adsorption Isothermal Lines From Three-component Solutions SOV/76-33-7-20/40

maximum. The component that is better adsorbed from the binary mixture is also better adsorbed from the three-component mixture. The absolute (AI) of the components of the systems under discussion are similar for each of the two employed adsorbents. There are 13 figures and 18 references, 15 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: January 9, 1958

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5(4) SOV/20-124-3-35/67

AUTHORS: Kiselev, A.V., Kovaleva, N. V., Korolev, A. Ya., Shcherbakova, K.D.

TITLE: The Chemical Modification of the Surface of Adsorbents and Its Influence on Adsorption Properties (Khimicheskoye modifitsirovaniye poverkhnosti adsorbentov i yego vliyaniye na adsorbtsionnyye svoystva)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 617-620 (USSR)

ABSTRACT: The present report deals with the chemical modification and variation of the adsorption properties of silica and graphite bodies. Highly dispersive silica aerosil and gas-black are used for this purpose. This modification was carried out for the purpose of rendering silica hydrophobic and of making soot hydrophilic. The first part of this paper deals with the modification of silica. Silica with a hydrated surface adsorbs polar substances well. By a reaction with silicon-organic compounds it is possible to modify the nature of their surface essentially in the direction of attaining a stable hydrophobic state, which is of practical interest for the application of silica as filling media for polymeric materials and as a thickening medium for lubricants. The modification consisted of a reaction of silica hydroxyl with trimethyl chlorosilane according to the scheme

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The Chemical Modification of the Surface of Adsorbents and Its Influence on Adsorption Properties

$$\begin{array}{ccccccc}
 & | & & & & | & \\
 & O & & CH_3 & & O & CH_3 \\
 & | & & | & & | & | \\
-O- & Si & -OH+Cl- & Si & -CH_3 \rightarrow -O- & Si & -O-Si-CH_3+HCl \\
 & | & & | & & | & | \\
 & O & & CH_3 & & O & CH_3 \\
 & | & & & & | &
\end{array}$$

Aerosil with a surface of about 150 m^2/g was treated for eight days at a temperature of 20^0 with saturated trimethyl chlorosilane vapor or with its solution in benzine. The greatest difference in the isothermal lines of adsorption is observed in steam. The adsorption of steam on a modified sample is several dozens of times lower than in the case of a normal sample. The isothermal line of the adsorption of steam on a modified sample is reversible, and it is not modified even after several months of contact with water, which is indicative of the strength of the surface compound formed. The second part of this paper deals with the formation of carbon black. The adsorption proper-

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SOV/20-124-3-35/67

The Chemical Modification of the Surface of Adsorbents and Its Influence on Adsorption Properties

ties of soot with respect to many adsorbed substances, especially with respect to polar ones, depend on the quantity of oxygen they contain. The authors modified gas black for the purpose of further graphitization. By annealing at more than 1500° the acid surface compounds are destroyed, the growth of graphite crystallites is promoted (chemical and crystallo-chemical modification) and the adsorption of the vapors of water, methanol, ammonia, methylamine, sulfur dioxide and other polar substances is considerably reduced. Thermal treatment, especially at temperatures of more than 2500°, makes the soot surface more homogeneous and prevents the adsorption of non-polar substances. Such a treatment of soot also increases its hydrophobic properties. An increase of the affinity of soot to polar substances, especially water, is of practical interest for polygraphical pigments and also for other polygraphically important cases. Also the nature of the surface and the colloid-chemical properties of soot are considerably modified by the oxide-treatment. The modi-

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SOV/20-124-3-35/67

The Chemical Modification of the Surface of Adsorbents and Their Influence on Adsorption Properties

fication of soot also modifies the adsorption of steam considerably. The variations of the corresponding isothermal lines are discussed. The double hysteresis found on this occasion is typical of the superposition of two phenomena, viz chemosorption and capillary condensation. The thermal treatment of soot and its oxidation in the liquid phase is able to modify soot to such an extent that the adsorption of steams on it is modified by dozens and hundreds of times of its amount. There are 2 figures and 25 references, 12 of which are Soviet.

PRESENTED: September 6, 1958, by M. M. Dubinin, Academician

SUBMITTED: September 5, 1958

Card 4/4

KISELEV, A. V.

~~5(4)~~ 5.1115 66497

AUTHORS: Babkin, I. Yu., Vasil'yeva, V. S., Drogaleva, I. V., Kiselev, A. V., Korolev, A. Ya., Shcherbakova, K. D. SOV/20-129-1-36/64

TITLE: The Effect of the Degree of Surface Modification of Silica by Trimethylchlorosilane on Its Absorptive Properties

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1, pp 131-134 (USSR)

ABSTRACT: In previous papers (Refs 1, 2) the authors showed that the physico-chemical surface properties of highly dispersed materials, such as carbon black or silica, can be influenced to a considerable degree by chemical reactions. The present paper reports on experiments carried out under the cooperation of L. I. Doroshina, M. G. Kuz'mina, G. M. Lyulina, and L. F. Pavlova, with the aim of reducing the adsorbing capacity of highly dispersed non-porous silica (aerosil) for hydrocarbons. To attain this, the aerosil surface was occupied with $Si(CH_3)_3$-groups. Since complete occupation is only possible on previously hydratized silica, the following samples were investigated: (1) the original aerosil -

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sample A1, (2) original aerosil, modified by treatment with trimethylchlorosilane - sample A1M, (3) aerosil hydratized in an autoclave - sample A1H, and (4) aerosil, hydratized in an autoclave, and then modified by treatment with trimethylchlorosilane - sample A1HM. The amount of trimethylsilyl-groups adhering to the silica surface was determined by means of microelementary analysis. The degree $\theta_{Si(CH_3)_3}$ to which the surface area is occupied is calculated from the size of the trimethylsilyl-groups (42 Å^2). The specific surface, its carbon content, and the degree to which it is occupied by trimethylsilyl-groups are shown in table 1. The effect of these groups lies in the fact that the interspaces between the groups, even when the surface is not occupied completely, but only in the manner of a mosaic - become so small that the larger hydrocarbon molecules are not able to penetrate to the surface. The adsorption isotherms for vapors of n-hexane, benzene, and methanol are given in figure 1, those for water in figure 2. The adsorption of hydrocarbons is decreased less than that of water on a 58% modified

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surface. 93% Modification produces a sharp decrease in the adsorbing capacity of the surface. The isotherm for heavy hydrocarbons becomes practically linear. This phenomenon may be of value for the chromatographic separation of hydrocarbon mixtures by means of gas adsorption. There are 2 figures, 1 table, and 11 references, 9 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov). Vsesoyuznyy nauchno-issledovatel'skiy institut aviatsionnykh materialov (All-Union Scientific Research Institute for Aviation Materials)

PRESENTED: June 13, 1959, by M. M. Dubinin, Academician

SUBMITTED: June 11, 1959

Card 3/3

KISELEV, A. V.

"The energy of adsorbate-adsorbent and adsorbate-adsorbate interactions in Monolayers on solid surfaces."

report to be submitted at Gordon Research Conferences - New London, New Hampton, and Meriden, N.H., 13 June-2 Sep 60.

Lomonsov University, Moscow.

KISELEV, A.V.

PHASE I BOOK EXPLOITATION SOV/4941

Mezhvuzovskoye soveshchaniye po khimii nefti, Moscow, 1956.

Sbornik trudov Mezhvuzovskogo soveshchaniya po khimii nefti (Collection of Transactions of the Inter-University Conference on Petroleum Chemistry) [Moscow] Izd-vo Mosk. univ., 1960. 313 p. Errata slip inserted. 1,600 copies printed.

Organizing Committee of the Conference: Chairman: B. A. Kazanskiy, Academician; Vice-Chairman: S. I. Khromov, Docent; G. M. Panchenkov, Professor; A. F. Plate, Professor; Secretary: Ye. S. Balenkova, Scientific Worker. Editorial Board: Resp. Ed.: A. F. Plate; I. V. Gostunskaya, I. N. Tits-Skvortsova, L. A. Erivanskaya.

PURPOSE: This collection of articles is intended for the teaching staff of universities and schools of higher education training specialists for the petroleum and petroleum-refining industries.

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COVERAGE: The collection includes articles dealing with the present state of the petroleum industry, the scientific research problems in petroleum chemistry, the chemistry of petroleum, the composition of petroleum and petroleum products, the scientific principles of refining petroleum into motor fuels and lubricants, and the manufacture of synthetic products from hydrocarbon gases and petroleum. One article discusses the effect of chemical composition and additives on fuel combustion in jet engines. The material was presented at the Inter-University Conference on Petroleum Chemistry, held at the Moscow State University imeni M. V. Lomonosov November 26-28, 1956. No personalities are mentioned. References accompany most of the articles.

TABLE OF CONTENTS: None given

The authors and the titles of articles are as follows:

Introduction by B. A. Kazanskiy, Academician

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Collection of Transactions (Cont.) SOV/4941

Kiselev, A. V., Laboratoriya adsorbtsii Moskovskogo gosudarstvennogo universiteta (Adsorption Laboratory of the Moscow State University) and Laboratoriya sorbtsionnykh protsessov Instituta fizicheskoy khimii AN SSSR (Laboratory of Sorption Processes, Institute of Physical Chemistry, AS USSR). Hydrocarbon Adsorption Energy 258

Paushkin, Ya. M., R. V. Sychev, T. P. Vishnyakova, and A. K. Zhomov, Moscow Petroleum Institute imeni I. M. Gubkin. Effect of Chemical Composition and Additives on Fuel Combustion in Jet Engines 293

AVAILABLE: Library of Congress (TP690.A1M445 1956)

JA/wrc/ec
4-20-61

~~Card 7/7~~

5.1190

77935
SOV/65-60-3-8/19

AUTHORS: Kiselev, A. V., Nikitin, Yu. S.

TITLE: The Effect of Production Conditions of Alumina-Silica Gels on Structure of Their Pores

PERIODICAL: Khimiya i tekhnologiya topliv i masel, 1960, Nr 3, pp 35-42 (USSR)

ABSTRACT: The structure of pores of alumina-silica gels was studied in relation to the amount of Al_2O_3 in catalysts prepared by the alumina method. The results of experiments are shown in Table 1. Four additional samples of alumina-silica gels were prepared from solutions of lower concentration containing two-fold lesser amount of dry substance. The results of analysis of their pores are shown in Table 2. There are 4 figures; 2 tables; and 15 references; 10 Soviet; 5 U.S. The 5 U.S. references are: Plank, C. J., Drake, L. C., J. Coll. Sci., 2, 399 (1947); Plank, C. J., J. Coll. Sci., 2, 413 (1947); Ashley, K. D., Innes, W. B., Ind. Eng. Chem., 44, 2,

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The Effect of Production Conditions of Alumina-Silica Gels on Structure of Their Pores

77935
SOV/65-60-3-8/19

857 (1952); Elkin, P. B., Shull, C. G., Roess, L. C., Ind. Eng. Chem., 37, 327 (1945); Tamele, M. W., Third World Petroleum Congress, 1951; Proceedings, Sect. 4, 98, Leiden, Brill (1951).

ASSOCIATION: All-Union Scientific Research Institute of Petroleum Industry and Moscow State University (VNII NP, MGU)

Vsesoyuznyy n.-i. inst. po pererabotke nefti i gaza i polucheniyu iskusstvennogo zhidkogo topliva i M.G.U.

Card 2/~~3~~ 2

AVGUL', N.N.; BERBZIN, G.I.; KISELEV, A.V.; LYGINA, I.A.

Adsorption and the heat of adsorption of n-pentane and n-hexane on barium sulfate. Izv. AN SSSR.Otd. khim. nauk no.11:1948-1954 N '60. (MIRA 13:11)

1. Institut fizicheskoy khimii AN SSSR.
(Heat of adsorption) (Pentane) (Hexane) (Barium sulfate)

68700
S/069/60/022/01/005/025
D034/D003

-56 5.4700
5.4400

AUTHORS: Kiselev, A.V. and Poshkus, D.P.

TITLE: The Heat and Entropy of Adsorption of Benzene and N--hexane Vapors on Magnesium Hydroxide

PERIODICAL: Kolloidnyy zhurnal, 1960, Vol XXII, Nr 1, pp 25-30 (USSR)

ABSTRACT: The authors report on a study intended to determine the heat and entropy of adsorption of benzene and n-hexane vapors on magnesium hydroxide with weakly dehydrated surface. As adsorbed the authors selected a $Mg(OH)_2$-3 specimen moderately freed of water at a temperature of 20^0 C. The differential heat of adsorbtion Q_a was determined from the isotherms of adsorption on the given specimen. The isotherms were determined at the temperatures T_1 and T_2 (10 and 30^0 C) according to the formula

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The Heat and Entropy of Adsorption of Benzene and N-hexane Vapors on Magnesium Hydroxide

$$Q_a = \frac{RT_1T_2}{T_2-T_1}\left[\ln\left(\frac{p}{p_s}\right)_{T_2} - \ln\left(\frac{p}{p_s}\right)_{T_1}\right]_a + L$$

(L - heat of condensation of the adsorbate; p/p_s - relative vapor pressure). The differential entropy of the transition of a mole of the adsorbate from the free liquid into the adsorption layer ΔSa was calculated according to the formula

$$\Delta S_a = -\frac{RT\left(\ln\frac{p}{p_s}\right)_{a,T} + \left(Q_a - L\right)}{T}$$

($T = 293.2^\circ$ (20° C); the magnitude $RT \ln \frac{p}{p_s}$, the differential work of adsorption at this temperature, to

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The Heat and Entropy of Adsorption of Benzene and N-hexane Vapors on Magnesium Hydroxide

be determined from isotherms as presented in a previous publication of the authors [Ref. 2]) The investigation has shown that the standard heat of adsorption of benzene vapors on the $Mg(HO)_2$-3 specimen is greater than the standard heat of adsorption of n-hexane vapors (graph 1). A comparison of the standard heats of adsorption on various adsorbents (table and graph 4) makes evident that the heat of adsorption of benzene vapors on polar adsorbents is greater or close to the heat of adsorption of hexane, whereas on a non-polar adsorbent the heat of adsorption of benzene is considerably below the heat of adsorption of n-hexane. The increase in the ratio of the heats of adsorption of benzene and n-hexane vapors on polar adsorbents as compared to this ratio on a non-polar

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The Heat and Entropy of Adsorption of Benzene and N-hexane Vapors on Magnesium Hydroxide

adsorbent (graphitized carbon black) is explained as due mainly to the stronger electrostatic interaction of benzene molecules, as compared to the interaction of hexane, with the electric field at the polar adsorbent surface. There are 4 graphs, 1 table and 13 references, 11 of which are Soviet, 1 English and 1 German.

ASSOCIATION: Moskovskiy universitet im. M.V. Lomonosova, Khimicheskiy fakul'tet, Laboratoriya adsorbtsii - Institut fizicheskoy khimii AN SSSR, Laboratoriya sorbtsionnykh protsessov (Moscow University im. M.V. Lomonosov, Chemical Department, Laboratory of Adsorption - Institute of Physical Chemistry AS USSR, Laboratory of Sorptive Processes)

SUBMITTED: September 3, 1958

Card 4/4

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000722730010-9"

S/069/60/022/03/10/019
B004/B007

AUTHORS: Kiselev, A. V., Pogosyan, T. A.

TITLE: The Theory of the Corpuscular Structure of Xerogels. 1. The Preparation of Silica Gels From Large Globules With Varying Number of Contacts and Their Investigation by the Adsorption Method

PERIODICAL: Kolloidnyy zhurnal, 1960, Vol. 22, No. 3, pp. 314 - 322

TEXT: The theory of the corpuscular structure of xerogels was developed by A. V. Kiselev in Refs. 1-5. Accordingly, the skeleton of xerogels consists of primary particles, which are spherical in the case of silica gels. The authors aim at producing brines with particles of such a size that their shape may be determined by means of an electron microscope, and that their behavior in the process brine - hydrogel - xerogel may be followed. The present paper describes the production of such brines and gels and the investigation of their adsorption properties. The brines were prepared by exchanging the sodium ion for the hydrogen ions in solutions of sodium silicate by means of the КУ-1 (KU-1) cation ex-

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The Theory of the Corpuscular Structure of Xerogels. 1. The Preparation of Silica Gels From Large Globules With Varying Number of Contacts and Their Investigation by the Adsorption Method

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B004/B007

changer. A description is given of the formation of germs in the silicic acid solution stabilized by alkali by means of heating, the addition of fresh silicic acid, and the formation of hydrogel by a small addition of HCl. The xerogels were obtained by drying at 110-120°C. Fig. 1 shows the methanol adsorption on eight xerogel samples which had been produced at various pH. The smallest specific surface was found in the case of xerogel obtained at pH=10.7 so that for the further experiments only brines with pH=10.7 were used. For the purpose of avoiding a structural change, the water was sublimated from the hydrogels in a vacuum according to N. M. Kamakin (Ref. 12). Then, the hydrogels were dried at 110-120°C. The adsorption isothermal lines for methanol- and benzene vapors were determined by means of an apparatus with a quartz spring scale (Fig. 2). The design of this apparatus had been begun by L. N. Soboleva (deceased). It was located in a TCП-4 (TSP-4) thermostat developed by G. G. Muttik in the authors' laboratory. Fig. 3 shows the benzene-adsorption isothermal lines for four silicahydrogels at 20°C, 150°C, and for the xerogels produced therefrom at 150°C. The

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The Theory of the Corpuscular Structure of Xerogels. 1. The Preparation of Silica Gels From Large Globules With Varying Number of Contacts and Their Investigation by the Adsorption Method

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specific surface was determined by B. G. Aristov by means of nitrogen adsorption at low temperatures. A table contains these values as well as the pore diameters and the number of contacts which, on the average, was 2.5. Fig. 4 shows that the specific sufface had not been changed by drying. During transition from hydrogel to xerogel merely a contraction of the pores occurs (Fig. 5). The samples obtained were homogeneously coarse-pored with a particle diameter of about 300 Å. The benzene-adsorption isothermal lines of silica gels are compared in Fig. 6 with those of quartz and further with the data for KCK-2 (KSK-2) silica gel obtained in the laboratory of the authors by Yu. A. El'tekov and D. P. Poshkus. Results of measurement show good agreement. Only at the stage of polymolecular adsorption and capillary condensation does the influence exerted by the packings of different densities become noticeable. There are 6 figures, 1 table, and 23 references: 18 Soviet and 5 English.

Moscow Univ im M.V. Lomonosov and Inst. Phys Chem AS USSR

Card 3/3

LYGIN, V.I.; KOVALEVA, N.V.; KAVTARADZE, N.N.; KISELEV, A.V.

Adsorption properties and infrared spectra of oxidized carbon blacks. Koll.zhur. 22 no.3:334-339 My-Je '60. (MIRA 13:7)

1. Institut fizicheskoy khimii AN SSSR, Moskva.
(Carbon black—Spectra) (Adsorption)

KISELEV, A.V.; LYGIN, V.I.

Infrared spectroscopic study of the physical adsorption of water on a hydrated silica gel surface. Koll. zhur. 22 no.4:403-410 Jl-Ag '60.
(MIRA 13:9)

1. Institut fizicheskoy khimii AN SSSR i Moskovskiy universitet im. M.V. Lomonosova, Khimicheskiy fakul'tet.
(Silica) (Adsorption)

5 115

S/069/60/022/006/002/008
B013/B066

AUTHORS: Kiselev, A. V., Korolev, A. Ya., Petrova, R. S., and Shcherbakova, K. D.

TITLE: Effect of the Degree of Chemical Modification of the Silica Surface With Tetramethyl Chloro Silane on the Adsorption of Nitrogen- and Krypton Vapors

PERIODICAL: Kolloidnyy zhurnal, 1960, Vol. 22, No. 6, pp. 671-679

TEXT: The authors of the present paper studied the effect of the silica surface modification on the adsorption of nitrogen- and krypton vapors. They achieved a considerable reduction of the interaction energy adsorbate - adsorbent by substituting trimethyl silyl groups for the hydrogen of the hydroxyl groups on the silicon dioxide surface. The adsorption of nitrogen- and krypton vapors was studied on five Aerosil samples. Aerosil is a non-porous, highly disperse silica which was treated with trimethyl chloro silane vapor of solution in benzine. To obtain samples modified as completely as possible, Aerosil is hydrated for 19.5 hours in the autoclave at 350°C and 169 atm with water, and then treated

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Effect of the Degree of Chemical Modification of the Silica Surface With Tetramethyl Chloro Silane on the Adsorption of Nitrogen- and Krypton Vapors

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with $ClSi(CH_3)_3$. This led to an up to 90% occupation of the Aerosil surface with $Si(CH_3)_3$ groups. The adsorption isotherms of nitrogen and krypton vapors were plotted at temperatures of liquid nitrogen. The adsorption of the two substances was found to be reduced by modifying the silica surface with trimethyl silyl groups. The krypton adsorption considerably decreases at a high degree of modification. Also the shape of the adsorption isotherms varies i.e., they are less bent. The isotherms for the above vapors are plotted in coordinates of the BET equation. It may be seen from it that owing to the reduction of the absolute adsorption quantity the BET equation is less satisfied, because with the less intense interaction of adsorbate - adsorbent, the interaction of adsorbate - adsorbate must not be neglected any longer. The specific surface for non-modified silica samples may be determined by the BET method, e.g. on the basis of the nitrogen vapor adsorption. For modified samples, however, the values obtained by the BET method are too low. It was found that the adsorption of nitrogen- and krypton vapors depends on the degree

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Effect of the Degree of Chemical Modification of the Silica Surface With Tetramethyl Chloro Silane on the Adsorption of Nitrogen- and Krypton Vapors

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of modification to such an extent that the BET method is not applicable for determining the specific surface of considerably modified samples. The adsorption isotherms obtained for the nitrogen and krypton vapors were compared with the isotherms previously obtained (Refs. 6,7,10) for vapors of n-hexane, benzene, methanol, and water (Fig. 3). Modification was shown to effect a considerable reduction of adsorption in all adsorbents. Fig. 4 illustrates the approximate course of the adsorption decrease at $p/p_s = 0.1$ with increasing occupation θ of the surface by $Si(CH_3)_3$ groups. V. P. Dreving is thanked for developing a volumetric apparatus, and B. G. Aristov for plotting the adsorption isotherms of nitrogen. There are 4 figures, 3 tables, and 35 references: 22 Soviet, 5 British, 4 US, and 3 German.

ASSOCIATION: Moskovskiy universitet im. M. V. Lomonosova Khimicheskiy fakul'tet, Laboratoriya adsorbtsii (Moscow University imeni M. V. Lomonosov, Chemical Division, Adsorption Laboratory)

Card 3/4
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S/076/60/034/012/001/027
B020/B067

AUTHORS: Poshkus, D. P. and Kiselev, A. V.

TITLE: Energy of Dispersion Interaction of Benzene and n-Hexane With the Surface of Magnesium Hydroxide

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 12, pp. 2640-2645

TEXT: In a preceding paper (Ref. 1), the authors assumed that the change in the ratio between the adsorption heats of benzene and n-hexane vapors on polar adsorbents is mainly due to the stronger electrostatic interaction of the benzene molecules as compared with the n-hexane molecules. Thus, an electric field is generated above the surface of the polar adsorbents, mainly above the lattice of $Mg(OH)_2$. Therefore, the authors studied the energy of interaction forces between benzene and n-hexane molecules and the $Mg(OH)_2$ surface. $Mg(OH)_2$ has a multi-layer rhombohedral ionic crystal lattice of the type CsI_2. Each lattice layer consists of an

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Energy of Dispersion Interaction of Benzene and n-Hexane With the Surface of Magnesium Hydroxide S/076/60/034/012/001/027 B020/B067

Mg ion plane which lies between two hydroxyl ion planes which, in turn, consist of oxygen and hydrogen ion planes. The Φ_{iD} potential of dispersion interaction of the member i of the chain of hydrocarbon molecules (CH_3, CH_2 and CH_{arom}) with the centers of force j of the $Mg(OH)_2$ lattice (H, O, and Mg) was calculated for three layers above the basal plane of $Mg(OH)_2$, i.e., 1) above the hydroxyl ion of the first (external) plane (layer A), 2) above the center of the hydroxyl-ion triangle of the first plane, below which lies the magnesium ion of the second plane (layer B), or 3) the hydroxyl ion of the third plane (layer C). When expanding the dispersion potential in a series, only the first two terms are considered which represent the potential of dipole - dipole and the dipole - quadrupole interactions. The others influence the entire potential only slightly. The constants of dispersion interaction were calculated. The sums of the exponential functions $\sum r_{ij}^{-n}$, where n = 6 and 8, and j = H, O, or Mg^{2+}, were calculated by assuming that a = 3.11 A, c = 4.73 A, u = 0.22, and that the distance

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Energy of Dispersion Interaction of Benzene and n-Hexane With the Surface of Magnesium Hydroxide S/076/60/034/012/001/027 B020/B067

between the hydrogen and oxygen atom centers in the hydroxyl ion is l_{OH^-} = 0.97 A. Summation was performed up to r_{ij} = 10 A. Hence, the great increase in the ratio between the adsorption heats of benzene and n-hexane on $Mg(OH)_2$ as compared to those of the vapors of these compounds on graphite is not caused by the dispersion interaction of benzene and n-hexane molecules with the basal plane of $Mg(OH)_2$. There are 3 figures, 5 tables, and 15 references: 6 Soviet, 2 US, 3 British, and 4 German.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov). Akademiya nauk SSSR, Institut fizicheskoy khimii (Academy of Sciences USSR, Institute of Physical Chemistry)

SUBMITTED: October 25, 1958

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S/076/60/034/012/002/027
B020/B067

AUTHORS: Poshkus, D. P. and Kiselev, A. V.

TITLE: Electrostatic Field Above the Basal Plane of Magnesium Hydroxide and Its Interaction With Benzene and n-Hexane Molecules

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 12, pp. 2646-2653

TEXT: In continuation of the calculation of the energies of dispersion interaction of benzene and n-hexane molecules with the $Mg(OH)_2$ basal plane, which was described in the preceding paper (Ref. 1) the authors studied the energy of electrostatic interaction of benzene and n-hexane molecules with the electric field above the $Mg(OH)_2$ basal plane. They determined the voltage component of the electric field F_z over the $Mg(OH)_2$ basal plane as depending on 1) the dipole moment of the OH ions, 2) the degree of homeopolarity of the bond between magnesium ions and

Electrostatic Field Above the Basal Plane of Magnesium Hydroxide and Its Interaction With Benzene and n-Hexane Molecules

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OH ions, 3) the distance z between two layers above this plane, i.e., a) over the OH ion and b) over the center of the triangle formed by the OH ions. The voltage of the electric field over the basal plane of $F_{z\varepsilon}$ ions (above the infinite hexagonal lattice of these ions) was calculated by summing the individual charges in the plane of such a lattice to a certain height. The values of $F_{z\varepsilon}/(\varepsilon/a^2)$ above the infinite two-dimensional hexagonal lattice of the point charges are given in Table 1. Fig. 1 shows the diagram $F_{z\varepsilon}/(\varepsilon/a^2)$ as a function of z/a. The values $F_{z\varepsilon}$ were determined from Fig. 1. Tables 2 and 3 give the calculated results for the voltage of the electric field above the two-dimensional, hexagonal lattice of the dipoles p of the hydroxyl ions perpendicular to the lattice plane, F_{zp}. Fig. 2 shows the voltage of the electric field F_z over the basal plane of $Mg(OH)_2$ with z = 2.6 Å as a function of the dipole moment p of the hydroxyl groups with two extreme states of the $Mg(OH)_2$ lattice. In Fig. 3 F_z over the basal plane of the $Mg(OH)_2$ lattice is graphically

Electrostatic Field Above the Basal Plane of Magnesium Hydroxide and Its Interaction With Benzene and n-Hexane Molecules

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represented as a function of the degree of homeopolarity of the bonds between Mg ions and OH ions. As an example, Table 4 shows the contributions of the negative charges and the dipoles of the first and second OH-ion planes and the positive charges of the Mg-ion surfaces of the first basal layer of $Mg(OH)_2$ to F_z above this layer, with z = 3.0 A and p = 2.4 D if a pure ionic bond exists between Mg- and OH ions. The voltage of the electric field above the basal plane depends only little on the homeopolarity of the ionic bonds Mg - OH whereas it strongly depends on the dipole moment of the OH ions, above all on the dipole moment of the OH ions on the surface. With increasing dipole moment the field voltage for both layers changes almost linearly. The voltage of the field above the OH ions has the opposite sign and its absolute value is approximately twice that of those above the center of the triangle formed by the OH ions. With increasing distance the electric field is gradually weakened. The induction interaction of benzene and n-hexane molecules with the basal plane of magnesium hydroxide cannot be caused by strong changes in the ratio of the absorption heats of benzene/n-hexane compared to that

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APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000722730010-9"

Electrostatic Field Above the Basal Plane of Magnesium Hydroxide and Its Interaction With Benzene and n-Hexane Molecules

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with graphite. These changes are due to the strong electrostatic interaction of the constant multipoles of the benzene molecules with the electric field above the $Mg(OH)_2$ basal plane. There are 4 figures, 4 tables, and 10 references: 7 Soviet, 2 British, and 1 Japanese.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences USSR). Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: October 25, 1958

Card 4/4

S/076/60/034/012/020/027
B020/B067

AUTHORS: Isirikyan, A. A. and Kiselev, A. V.

TITLE: Adsorption Heats of Hydrocarbons on Magnesium Oxide

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 12, pp. 2817-2824

TEXT: In this paper, the complete values of the adsorption heats of n-hexane and benzene on magnesium oxide are given, which in an earlier paper (Ref. 2) had been used for a comparison with the theoretically calculated values. The measurement results of the isothermal lines and the differential heats of adsorption of the vapors on benzene, n-hexane, and n-octane on MgO are evaluated. The calorimetric determination of the heats of adsorption was made in an apparatus described in Refs. 13 and 14. The results are shown in Figs. 1-3. The adsorption of n-hexane and benzene vapors was studied until the formation of approximately two adsorption layers, whereas the adsorption of n-octane vapors was studied almost until saturation. This allowed the determination of the maximum desorption temperature near the saturation and the calculation of the distribution of

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2

Adsorption Heats of Hydrocarbons on Magnesium Oxide

S/076/60/034/012/020/027
B020/B067

the pore volumes from the desorption branch of the isotherm. When determining the absolute values of adsorption per surface unit, the specific surface s must be known which, in turn, is determined from the surface ω_0 that is occupied by the molecule adsorbed in the monomolecular layer. By using the equations of Langmuir, BET or other varieties the isothermal lines of adsorption can be evaluated to determine the capacity of the monolayer a_m or the energetic characteristics of the system investigated. The values thus obtained are, however, often contradictory. The constants of the equations BET and of Hüttig for the isothermal lines of adsorption of the benzene, n-hexane, and n-octane vapors on MgO are listed in Table 1. Table 2 gives the values ω_0 for hydrocarbons, which were calculated by various methods. Fig. 4 shows the heats of adsorption of the benzene, n-hexane and n-octane vapors on MgO as depending on the surface filling. Fig. 5 shows the differential entropies of adsorption for the systems investigated (standard state - normal liquid), and Fig. 6 gives a comparison of the isothermal lines of the dependence of the adsorption heats and the adsorption on the relative vapor pressure of octane on coarse-pored MgO. There are 6 figures, 2 tables, and 27 references: 20 Soviet, 3 US, 3 British, and 3 German.

Card 2/2 Moscow State U., Chemistry Faculty

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S/020/60/132/04/39/064
B004/B007

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AUTHORS: Kiselev, A. V., Poshkus, D. P.

TITLE: Statistical Thermodynamic Calculation of the Adsorption Equilibrium of Argon on Graphite

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 4, pp. 876-879

TEXT: The present paper aims at approximately calculating the change $\Delta\mu$ in the chemical potential of argon occurring in the adsorption on the base of graphite in the case of a low degree of surface occupation θ. The authors write down the state function (1) for the adsorbed molecules, and derive equation (2) for $\Delta\mu$. They discuss the Hamiltonian (6) for the adsorbed argon atom, and calculate the equilibrium distance z_o of the center of the argon atom from the first plane of the centers of the carbon atoms of the graphite lattice (Table 1). Further, equation (12) is written down for the quantum-mechanical factor ν^{**}, and the quantity ω_m of the hexagonal or quadratic packing of the argon atoms on the surface is determined according to Ref. 16. The following are the results: $\Delta\mu$ =

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BEREZIN, G.I.; KISELEV, A.V.; SINITSYN, V.A.

Heat capacity of the adsorption system silica gel - water. Dokl. AN SSSR 135 no.3:638-641 N '60. (MIRA 13:12)

1. Institut fizicheskoy khimii Akademii nauk SSSR. Predstavleno akad. V.I. Spitsynym.
(Heat capacity) (Silica)

KISELEV, A. V.

"The Chemical Modification of the Surface of Adsorbents and Their Application in Gas Chromatography."

report to be submitted for the Third East German Symposium in Gas Chromatography, Schkopau, East Germany, 16-19 May 1961

Moscow sTate University, Lab. of Adsorption.

KISELEV, A. V. Prof

"On Chemical Modification of highly dispersed substances (fillers and adsorbents"

report presented at the General Conference of the Division of Chemical Sciences of the Academy of Sciences, USSR, 27-28 October 1960

So: Izvestiya Akademii nauk SSSR, otdeleniye khimicheskikh nauk, No. 2 1961, Moscow, pages 378-380

KISELEV, A. V.

report to be submitted for the IUPAC 21st Conference and 13th Intl. Congress of Pure and Applied Chemistry, Montreal, Canada, 2-12 August 1961

GORODISKIY, O. V., Academy of Sciences UkSSR, Kiev - "The oscillographic investigation of the electrochemical kinetics in fused salts" (Section A.3,e.2 - Session I, 11 Aug 61, afternoon)

GURVICH, L. V., Academy of Sciences USSR, Moscow - "The calculation of thermodynamic functions of gases in a wide temperature range" (Section A.3,c,(1), Session II - 8 Aug 61, afternoon)

KARGIN, V. A., Physico-Chemical Institute imeni L. Ya. Karpov, Moscow - "Vitrification phenomena in crystallin polymers" (Section B.4 - 7 Aug 61, afternoon)

KISELEV, A. V., Moscow State University imeni M. V. Lomonosov - "The influence of surface heterogeneity and adsorbate-adsorbate interaction on the adsorption properties of solid surfaces" (Joint Session, Sections A.2 and B.1 - 8 Aug 61, morning)

KONDRAT'YEV, V. N., Institute of Chemical Physics, Academy of Sciences USSR, Moscow - "The HO_2 radical" (Section A.1, Session I - 11 Aug 61, morning) (Also, Section A.1, Chairman, Session I - 8 Aug 61, morning)

KUZNETSOV, V. I., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "A novelty in the use of organic co-precipitants for concentration of small amounts of the elements" (To be presented in Russian) (Section C.2 - 11 Aug 61, morning)

LAVRUKHINA, A. K., RAKOVSKIY, E. E., and MOSKALEVA, L. P., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "New data on radiochemical investigations of the processes of fission and fragmentation induced by high energy protons" (Section A.4 - 8 Aug 61, afternoon)

LOVACHEV, L. A., Academy of Sciences USSR, Moscow - "Determination of rate constants of elementary processes from flame velocities as a function of temperature, pressure, and molecular transfer coefficients" (Section A.3,b,(2) - 7 Aug 61, afternoon)

MENDIATH, S. (Probably MINDYATH, S.) and GERASIMOV, Y. I., Moscow State University imeni M. V. Lomonosov - "Study of the thermodynamic properties of the system iron-latinum" (Section A.3,c,(3), Session II(A) - 11 Aug 61, morning)

PANCHENKOV, G. M., KOLCHIN, A. M., MALAKOV, V. F., and SEMENOV, Ya., Moscow State University imeni M. V. Lomonosov - "Emission of complex ions in solid-phase reactions" (Joint Session, Sections A.2 and B.1, 8 Aug 61, morning)

SEMENOV, N. N., Institute of Chemical Physics, Academy of Sciences USSR, Moscow - "Certain chemical reactions at reduced temperatures and related problems of energy transfer" (To be presented in Russian) (Plenary lecture - Saturday, 12 Aug 61)

SHILOV, Ye. A., Academy of Sciences UkSSR, Kiev - "The active agents and the intermediary complexes in the heterolytic reactions of halogenation of the organic compounds" (Section A.1, Session II - 11 Aug 61, morning)

SMIRNOV, M. V., Electrochemistry Institute, Sverdlovsk - "The equilibrium between the titanium subgroup metals and the salt melts" (Section B.3 - 7 Aug 61, afternoon)

TAL'ROZE, V. L., Institute of Chemical Physics, Academy of Sciences USSR - "Reactions of ions and molecules in the gas phase" (Section A.1, Session I - 9 Aug 61, afternoon)

TERENIN, Aleksandr N., Leningrad State University imeni A. A. Zhdanov - (Section A.1, Chairman, Session I - 8 Aug 61, afternoon Session) (Also on program for Section A.1, Session I - 9 Aug 61, afternoon)

TERENIN, Aleksandr N., VILESOV, F. I., KURBATOV, B. L., and DOKUCHAYEVA, N. I., Leningrad State University imeni A. A. Zhdanov - "Mass-spectrometry and luminescence of radicals in the photodissociation and photoionization of molecules by vacuum ultra-violet radiation" (Section A.1, Session I - 9 Aug 61 - afternoon)

TUNITSKIY, N. N., Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov - "On the dissociation of molecules on electron impact and the early states of radiation-chemical processes" (Section A.1, Session I - 8 Aug 61, afternoon)

YANSHEKHIN, Emmanuil Ye., and KOROLEV, V. V., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Moscow - "The plasma generator and its use for spectral analysis of alloys and rocks" (Section C.1 - 8 Aug 61, morning)

VINOGRADOV, A. P., LAVRUKHINA, A. K., and REVINA, L. D., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "The study of nuclear reactions in iron meteorites under the action of high energy protons" (Section A.4 - 8 Aug 61, afternoon)

YAKOVLEV, Yu. V., and ALIMARIN, I. P., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "The determination of trace impurities in some materials for semiconductor techniques by radio-activation analysis" (To be presented in Russian) (Section C.1 - 8 Aug 61, afternoon)

YEROFEYEV, Boris V., Institute of Physical-Organic Chemistry, Minsk - "The effect of donor and acceptor admixtures on the decomposition rate of solids" (Section A.2 - 8 Aug 61, afternoon)

AVGUL', N.N.; BEREZIN, G.I.; KISELEV, A.V.; LYGINA, I.A.

Adsorption and heat of adsorption of normal alcohols on graphitized carbon black. Izv. AN SSSR. Otd. khim. nauk no.2:205-214 F '61. (MIRA 14:2)

1. Institut fizicheskoy khimii AN SSSR.
(Adsorption) (Carbon black) (Alcohols)

AVGUL', N.N.; KISELEV, A.V.; LYGINA, I.A.

Adsorption energy of CO_2, SO_2, $(CH_3)_2CO$ and $(C_2H_5)_2O$ on graphite. Izv. AN SSSR. Otd.khim.nauk no.8:1395-1403 Ag '61. (MIRA 14:8)

1. Institut fizicheskoy khimii AN SSSR.
(Adsorption)

AVGUL', N.N.; KISELEV, A.V.; LYGINA, I.A.

Adsorption energy of water, alcohols, ammonia, and methylamine on graphite. Izv. AN SSSR. Otd.khim.nauk no.8:1404-1411 Ag '61. (MIRA 14:8)

1. Institut fizicheskoy khimii AN SSSR.
(Adsorption)

AVGUL', N.N.; KISELEV, A.V.; LYGINA, I.A.

Adsorption and heat of adsorption of diethyl ether, acetone, and acetic acid vapors on graphitized carbon black. Izv. AN SSSR Otd.khim.nauk no.12:2116-2125 D '61. (MIRA 14:11)

1. Institut fizicheskoy khimii AN SSSR.
(Adsorption) (Ethers) (Acetone) (Acetic acid)

KISELEV, A.V.; PAVLOVA, L.F.

Adsorption from benzene - hexane solutions by means of the 5A molecular sieve. Kin.i kat. 2 no.4:599-605 Jl-Ag '61. (MIRA 14:10)

1. Institut fizicheskoy khimii AN SSSR i Moskovskiy gosudarstvennyy universitet imeni M.V.Lomonosova, khimicheskiy fakul'tet.
(Adsorption)

KISELEV, A.V.

Modification of a solid for the gas chromatography of the adsorbent as a carrier and a capillary. Vest.Mosk.Un.Ser.2:Khim. 16 no.5: 31-51 S-O '61. (MIRA 14:9)

1. Laboratoriya adsorbtsii i gazovoy khromatografii Moskovskogo universiteta.

(Gas chromatography)

S/069/61/023/001/005/009
B124/B204

AUTHORS: Isirikyan, A. A. and Kiselev, A. V.

TITLE: Effect of compression of carbon black on the isothermal line and heat of adsorption of n-hexane

PERIODICAL: Kolloidnyy zhurnal, v. 23, no. 1, 1961, 67-75

TEXT: The aim of the present paper is an explanation of the nature of inhomogeneities arising in carbon black compression, as well as of their effect upon the isothermal line and heat of adsorption of vaporous hydrocarbons. Сферон-6 (sferon-6) canal lampblack annealed in a helium atmosphere at 2800°, as used in the work under Ref. 17, was used as an adsorbent. This sample was compressed in a mechanical press at pressures of up to 4 and up to 10 t/cm^2. The resulting isothermal lines of adsorption are illustrated in Figs. 1 and 2. Table 1 shows the specific surfaces as determined from the isothermal line of n-hexane adsorption by the BET method; the specific surface determined by the authors agrees well with published values. The limiting volume V_s of sorption (bulk volume of the pores) decreases rapidly already at a relatively soft compression

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(4 t/cm^2), whereas it varies only slightly with further compression up to 10 t/cm^2. The coordination number n displays the same character (Table 1). The absolute isothermal lines of adsorption and the curves of adsorption heat obtained for the range of monomolecular filling and transition to polymolecular filling are shown in Fig. 2 (below) and Fig. 3. Table 2 presents the standard differential thermodynamic characteristics of n-hexane adsorption corresponding to a 50% filling of the monolayer Θ=0.5 upon sferon-6 carbon black (annealed at 1700°C in a hydrogen stream) and upon the carbon black samples of the authors. At 1700°C, channel was graphitized only to a slight extent since the adsorption energy of n-hexane during a heating of the carbon black to 2800°C rose by 0.25 kcal/mole, whereas the adsorption entropy in the same case decreased by 0.68 units of entropy. For comparison, Fig. 3 shows also the curve of the differential adsorption heat of n-hexane on P-33 (R-33) carbon black heated to only 1000°C. The arrows indicate the direction of the curve of differential adsorption heat upon non-porous carbon black with a homogeneous surface in the case of compression. Fig. 4 shows the heat difference in capillary condensation of n-hexane upon compressed and uncompressed carbon black

samples. The values of the wetting energy ΔA, heat of wetting Q_l, entropy of wetting ΔS_l, and the mean molar entropy variation ΔS_m during adsorption of the monolayer are compiled in Table 3. Table 4 shows that the fluctuations of the quantities S'_Q, when the value of a_h (adsorption value) is chosen between 0.4 and 0.6 mmole/g, are smaller than the corresponding variations of s'_A. For this reason, results from heat measurement are more reliable. The authors proved that the maxima of the heat of capillary condensation at the end of sorption depend on the geometrical structure of the adsorbent only, and that they occur at the end of capillary condensation when porosity is sufficiently uniform. There are 4 figures, 4 tables, and 18 references: 13 Soviet-bloc and 5 non-Soviet-bloc.

ASSOCIATION: Moskovskiy universitet im. Lomonosova, Khimicheskiy fakul'tet, Laboratoriya adsorptsii (Moscow University imeni Lomonosov, Division of Chemistry, Laboratory of Adsorption)

SUBMITTED: October 12, 1959

S/069/61/023/002/002/008
B101/B208

AUTHORS: Kiselev, A. V. and Khrapova, Ye. V.

TITLE: Approximate expression for the wave-like isotherms of nitrogen adsorption on graphitized carbon black, considering adsorbate-adsorbate interaction in the first and second layers

PERIODICAL: Kolloidnyy zhurnal, v. 23, no. 2, 1961, 163-169

TEXT: It was shown in previous papers (Ref. 1: Kolloidn. zh., 19, 572, 1957; Ref. 2: ibid., 20, 444, 1958) that the adsorption isotherm of vapors, particularly of nitrogen, begins with a concave section owing to adsorbate-adsorbate interaction. For the first section of the prevalent occupation of the monolayer, the following equation is written:
$h = \theta/K_1'(1 - \theta)(1 + K_n\theta)$ (1), while the approximate equation
$h = \theta(1 - h)^2/K_1'\left[1 - \theta(1 - h)\right]\left[1 + K_n\theta(1 - h)\right]$ (2) holds for the transition to the adsorption of the second layer. h denotes the relative pressure, θ the total degree of surface occupation, K_1' the equilibrium constant for the adsorbate-adsorbent interaction, and K_n the equilibrium constant for the

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adsorbate-adsorbate interaction. The authors studied the adsorption of nitrogen vapor in a wide range of θ, and tried to obtain a better approximation of equation (2) to the wave-like course of the adsorption isotherm. Adsorption of N_2 was performed at $-195^{\circ}C$ on Soviet T-1 (T-1) carbon black (annealed at $3000^{\circ}C$; specific surface s - 28.1 m^2/g), and T-2 (T-2) ($3200^{\circ}C$, s = 6.9 m^2/g) by means of an apparatus which has already been described by the authors (Ref. 15: Izv. AN SSSR, Otd. khim. n., 1958, 390). Fig. 1 gives the results and compares them with those obtained by S. Ross, W. Winkler (Ref. 3, see below), and S. Ross, W. W. Pultz (Ref. 4, see below). The waves of the isotherm of successive occupation of the black surface first with the monomolecular nitrogen layer and then with the following layers are given by $\theta'' = (\alpha - \alpha_m)/\alpha_m$, where $\alpha_m = 10.2_5$ μmole/m^2, is the occupation of the monomolecular layer; $\theta''' = (\alpha - \alpha_2)/\alpha_m$ with $\alpha_2 = 18.0$ μmole/m^2 is the occupation of the second layer. These parts of the isotherm are expressed by Eq. (2) if for each part another value of the constants is taken. This is shown in Fig. 4. The constants thus calculated are presented in Table 2. Fig. 5 shows that agreement was brought about between calculation and experimental data by substituting the various values for the constants of

the individual sections. There are 5 figures, 2 tables, and 19 references: 8 Soviet-bloc and 11 non-Soviet-bloc. The 3 references to English-language publications read as follows: Ref. 3: S. Ross, W. Winkler, J. Colloid. Sci., 10, 319, 1955; Ref. 4: S. Ross, W. W. Pultz, J. Colloid. Sci., 13, 397, 1958; Ref. 12: G. D. Halsey, J. Amer. Chem. Soc., 74, 1082, 1952.

ASSOCIATION: Moskovskiy universitet, Khimicheskiy fakul'tet, Laboratoriya adsorptsii (Moscow University, Chemical Division, Laboratory of Adsorption)

SUBMITTED: October 7, 1959

AVGUL', N.N.; KISELEV, A.V.; LYGINA, I.A.

Isotherms and heats of adsorption of alcohols on carbon blacks of various degrees of graphitization [with summary in English]. Koll.zhur. 23 no.4:369-375 Jl-Ag '61. (MIRA 14:8)

1. Institut fizicheskoy khimii AN SSSR, Gruppa khimii poverkhnosti, Moskva.
(Alcohols) (Heat of adsorption)

BEZUS, A.G.; DREVING, V.P.; KISELEV, A.V.

Isotherms and heats of adsorption of propane and propylene on graphitized carbon black. Energy of the adsorption forces [with summary in English]. Koll.zhur. 23 no.4:389-398 Jl-Ag '61. (MIRA 14:8)

1. Moskovskiy universitet, Khimicheskiy fakul'tet, Laboratoriya adsorbtsii.

(Propane—Thermal properties) (Propene—Thermal properties) (Heat of adsorption)

DZHIGIT, O.M.; KISELEV, A.V.; MUTTIK, G.G.

Heats of adsorption of p-diethyl ether on silica gel [with summary in English]. Koll.zhur. 23 no.4:504-505 Jl-Ag '61.
(MIRA 14:8)

1. Moskovskiy universitet im. M.V. Lomonosova.
(Esther) (Heat of adsorption)

AVGUL', N.N.; KISELEV, A.V.; LYGINA, I.A.

Adsorption and heat of adsorption of isomeric butanols on graphitized carbon black. Koll.zhur. 23 no.5:513-520 S-O '61. (MIRA 14:9)

1. Institut fizicheskoy khimii AN SSSR, Gruppa khimii poverkhnosti, Moskva.
(Butyl alcohol) (Heat of adsorption)

DZHIGIT, O.M.; KISELEV, A.V.; MUTTIK, G.G.

Heat of adsorption of water vapor on silica gel with hydrated and dehydrated surfaces. Koll.zhur. 23 no.5:553-562 S-O '61. (MIRA 14:9)

1. Moskovskiy universitet, Khimicheskiy fakul'tet, Laboratoriya adsorbtsii.
(Water vapor) (Silica) (Heat of adsorption)

KISELEV, A.V.; LYGIN, V.I.

Infrared spectroscopy study of benzene and hexane adsorption on silica. Koll.zhur. 23 no.5:574-581 S-O '61. (MIRA 14:9)

1. Moskovskiy universitet, Khimicheskiy fakul'tet, Institut fizicheskoy khimii AN SSSR.
(Adsorption) (Spectrum, Infrared)
(Hydrocarbons)

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S/069/61/023/005/005/008
B124/B101

AUTHORS: Kiselev, A. V., Kovaleva, N. V., Korolev, A. Ya.

TITLE: Adsorptive properties of oxidized carbon blacks. 1. Oxidation of channel black in an aqueous medium

PERIODICAL: Kolloidnyy zhurnal, v. 23, no. 5, 1961, 582 - 591

TEXT: In this paper, the adsorptive power of channel gas carbon black samples from Ukhta with a specific surface of about 150 m^2/g and an oxygen content of 4.4% which had been oxidized in aqueous solution without heating with sodium hypochlorite, hydrogen peroxide, and a mixture of HNO_3 and H_2SO_4, was investigated. The chemisorbed-oxygen content, hydrophilic properties, and wettability of the carbon black are increased by polar organic liquids. The carbon black forms highly disperse colloidal hydrosols without addition of organic wetting agents. After drying and removing substances adsorbed on carbon black by exhaustion at 150°C, the C and H contents were determined by a microanalytical technique, and the total oxygen content was established

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from the difference. The presence of active oxygen was detected by adsorption of NaOH from the aqueous solution and by determining the content of hydroxyl or phenol groups according to Grignard. The volatile substances content was determined by heating the carbon black to 820°C. The nitrogen content in the carbon black samples treated with the $HNO_3 - H_2SO_4$ mixture was determined by the Kjeldahl technique, and was found to be 0.27%. The specific surface was calculated from the adsorption isotherms of nitrogen vapor at the boiling point of nitrogen according to BET. Data on the specific surface and the chemical composition of carbon blacks oxidized by various techniques are given in a table. The oxidation of the carbon black surface leads to a reduced adsorption of n-hexane vapor. This is due to the fact that the oxidized surface is covered with oxygen-containing groups so tightly that there is no more room available for the large n-hexane molecules. The increase in the adsorptive power for benzene vapor with the oxidation degree of the carbon black surface is due to the fact that the interaction of the π-bonds in the benzene molecules with the OH groups on the surface of oxidized carbon black samples is intensified. The difference between oxidized and non-oxidized carbon black surfaces

becomes still more pronounced when methanol and water vapors (Fig. 2) are adsorbed. Methanol is probably chemically sorbed, too. The carbon black surface modified by graphitization or oxidation which becomes either strongly hydrophobe or strongly hydrophilic, can change the adsorption of water vapor by one or two orders of magnitude. Methanol vapor is most strongly adsorbed on surfaces oxidized with an HNO_3-H_2SO_4 mixture, although these samples contain less oxygen than samples oxidized with NaOCl; the same holds for the adsorption of water vapor. The adsorption of all vapors investigated generally increases with the degree of oxidation. The authors thank G. M. Lyulina, N. N. Avgul', A. P. Arkhipova, L. I. Doroshina, and M. G. Kuz'mina for assistance. There are 5 figures, 1 table, and 20 references: 13 Soviet and 7 non-Soviet. The two most recent references to English-language publications read as follows: M. L. Studebaker, E. Hoffman, A. C. Wolfe, L. G. Nabors, Industr. and Engng. Chem. 48, 162, 1956; J. V. Hallum, H. V. Drushell, J. Phys. Chem. 61, 110, 1958.

ASSOCIATION: Institut fizicheskoy khimii AN SSSR, Gruppa khimii poverknosti Moskva (Institute of Physical Chemistry AS USSR, Group of Surface Chemistry, Moscow)

BEREZIN, G.I.; KISELEV, A.V.; SINITSYN, V.A.

Dependence of the average molar heat capacity of an adsorbate on the differential heat of adsorption. Koll.zhur. 23 no.5: 638-639 S-O '61. (MIRA 14:9)

1. Institut fizicheskoy khimii AN SSSR, Gruppa khimii poverkhnosti, Moskva.
(Heat of adsorption) (Heat capacity)
(Systems (Chemistry))

S/076/61/035/002/001/015
B124/B202

AUTHOR: Kiselev, A. V.

TITLE: Energy of interaction adsorbate - adsorbent and adsorbate - adsorbate in monolayers on the surfaces of solids. Adsorption heat and adsorption equilibrium

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 2, 1961, 233-257

TEXT: The author mainly discusses methods of approximation calculations of adsorption heats and equilibria as well as some results obtained herewith. He first deals with the adsorption of simple nonpolar molecules on the basal plane of graphite. The potential adsorption energy of an isolated adsorbate molecule or its center of forces i with the centers of forces of the adsorbent j was calculated from the equation

$$\Phi_{ij}(z) = -C_1 \sum_j r_{ij}^{-6}(z) - C_2 \sum_j r_{ij}^{-8}(z) - C_3 \sum_j r_{ij}^{-10}(z) + B' \sum_j e^{-r_{ij}/\varrho}. \quad (1)$$

where z is the distance of the center i from the plane which passes through

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the centers of the carbon atoms of the external basal plane; r_{ij} is the distance of the center i from the center j of the graphite lattice, C_1, C_2, and C_3 are the constants of the electrochemical attraction of type dipole - dipole, dipole - quadrupole, and quadrupole - quadrupole, and ϱ is the constant of repulsion. C_1 was calculated from the Kirkwood-Müller equation by means of the polarizability and the magnetic susceptibility of the centers i and j, C_2 and C_3 were calculated in the same way, ϱ was obtained from the corresponding lattice constants ϱ_i and ϱ_j, and, finally, B' was obtained from the equilibrium condition $(\partial\Phi(z)/\partial z)_{z=z_0} = 0$ (2).

The potential of the interaction adsorbate - adsorbate for nonpolar molecules Φ_{ij} was determined from the equation

$$\Phi_{ii} = -\frac{1}{2}\sum_i \varphi_{ii} = \frac{1}{2}\left(-C_{ii}\sum_i r_{ii}^{-6} + b_{ii}\sum_i r_{ii}^{-12}\right), \quad (3),$$

where Φ_{ij} is the potential of the interaction between two isolated centers i and r_{ii} the distance of these centers. The constant of repulsion was determined from the equilibrium condition at values of r_{ii} which

correspond to a degree of surface filling $\Theta=1$; at $\Theta=0.5$ the repulsion energy in Φ_{ij} may be neglected. Table 1 shows a comparison of the calculated values Φ^{0} and the measured differential heats of adsorption Q_a^0 at $\Theta=0.5$. Good agreement was obtained. When studying the adsorption of complex nonpolar molecules on the basal plane of graphite the adsorption energy was determined as the sum of the adsorption energies of their individual links i by taking account of the different distances z_i of the different links i from the plane xy(z=0) for the most favorable surface orientation of the molecules. For n-alkanes with n carbon atoms in the molecule

$$\Phi = 2\Phi_{CH_3} + (n-2)\Phi_{CH_2} = 2(\Phi_{CH_3} - \Phi_{CH_2}) + n\Phi_{CH_2} = a + bn. \quad (4)$$

holds from which the relation $-\Phi'_{n-alk} = 0.85 + 1.88n$(kcal/mole) (5) is obtained for n-alkanes and $-\Phi'_{\alpha-monool} = -0.2 + 1.88n$(kcal/mole) for α-monoolefines. Table 2 compares the calculated values of $-\Phi^{0}$ with the measured values of Q_a^0 (for $\Theta = 0.5$) for some isoalkanes, cyclanes, and aromatic hydrocarbons. The author also deals with the adsorption of polar

molecules on the basal plane of graphite. Table 3 shows a comparison of the values $-\Phi$ calculated for $\Theta = 0$ and $\Theta = 1$ with the adsorption heats. When calculating $-\Phi_0$ the electrokinetic attraction and the energy of electrostatic inductive attraction $\alpha_j \mu_i^2 \sum_j r_{ij}^{-6}$ were taken into account. Table 4 shows a comparison of the adsorption energy and the adsorption heats of water, alcohols, ammonia, and methylamine. In this case both the electrokinetic and the electrostatic (inductive) interaction of the molecules with the carbon atoms of the graphite lattice and the different degree of their mutual association at the expense of the hydrogen bond were taken into account. In connection with the adsorption of nonpolar molecules on ion crystals the author compared the calculated values of potential adsorption energy $-\Phi$ with those measured in the calorimeter and calculated from the isoster (Table 5). The author then discusses the adsorption of n-hexane and of benzene on magnesium hydroxide and the adsorption of silicic acid and silicon dioxide. Table 6 compares the shifts $\Delta\nu$ of the oscillation frequency of the hydroxyl groups on the surface with the differences of adsorption heat Q_a

and Q_s (for $\Theta \approx 0.5$). In this case, the order of the quantities $\Delta\nu$ and Q_s is in qualitative agreement. The author also discusses adsorption on chemically modified surfaces. In the theoretical calculation of the equilibrium constant the author first determines the potential curves of the interaction adsorbate - adsorbent and adsorbate - adsorbate. In the following he calculates the distribution functions of the system adsorbent-adsorbate by the methods of statistical mechanics by using certain dynamical models in the adsorption complex. Polyani and D. P. Poshkus are mentioned. The present paper was presented at the Gordon Conference on Surface Chemistry, Meriden (New Hampshire, USA), July 4, 1960. There are 18 figures, 6 tables, and 77 references: 47 Soviet-bloc and 30 non-Soviet-bloc; E. L. Pace, A. R. Siebert, J. Phys. Chem. 64, 961, 1960.

ASSOCIATION: Akademiya nauk SSSR, Institut fizicheskoy khimii (Academy of Sciences USSR, Institute of Physical Chemistry); Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova, Khimicheskiy fakul'tet (Moscow State University imeni M. V. Lomonosov, Division of Chemistry)

KISELEV, A.V.

Gordon conference on interfacial chemistry in the U.S.A. held on July 4-8, 1960. Zhur. fiz. khim. 35 no.2:476-477 F '61. (MIRA 16:7)

(Surface chemistry—Congresses)

KALMANOVSKIY, V.I.; KISELEV, A.V.; LEBEDEV, V.P.; SAVINOV, I.M.; SMIRNOV, N.Ya.; FIKS, M.M.; SHCHERBAKOVA, K.D.

Gas chromatography in glass capillary columns with a chemically modified surface. Zhur.fiz.khim. 35 no.6:1386-1388 Je '61. (MIRA 14:7)

1. Moskovskiy gosudarstvennyy universitet imeni M.V.Lomonosova i Dzerzhinskiy filial opytno-konstruktorskogo byuro avtomatiki Goskhimkomiteta.

(Gas chromatography)

S/076/61/035/008/016/016
B110/B101

AUTHORS: Vasil'yeva, V. S., Kiselev, A. V., Nikitin, Yu. S., Petrova, R. S., and Shcherbakova, K. D.

TITLE: Graphitized carbon black as adsorbent in gas chromatography

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 8, 1961, 1889 - 1891

TEXT: In the work under consideration, the authors made use of geometrically and chemically modified silica gel as the carrier of another solid body. Thermal types of carbon black annealed at ~ 3000°C are high-disperse bodies with a very homogeneous surface. Their absolute adsorption values are much greater than those of other adsorbents. Tablets are difficult to produce without binding agents. Therefore, the carbon black is introduced into the large pores of the solid carrier. Thus, a powdery adsorbent with homogeneous surface may be introduced into the column. The carrier should be a large-porous body with thermally and chemically stable and very poorly adsorbing surface. In the present case, the authors used large-porous silica gel with a very small surface covered by chemically grafted trimethyl silyl groups. A 2-hr hydrothermal treatment in the

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autoclave at 350°C reduced the silica gel surface to 15 m^2/g; the enlargement of skeleton globules and pores was established by electron microscopy. Further grafts of trimethyl silyl groups on the silica gel surface according to I. V. Borisenko led to a sharp decrease of adsorption. ~18% blown out and sieved graphitized thermal carbon black T-1 (T-1) (3000°C) was then introduced into the pores. The silica gel was thereupon introduced into the column chromatograph, where it was heated for 2 hr in the nitrogen flow at 150°C. Graph a) in the figure shows chromatograms of vapor mixtures of benzene, acetone, and n-hexane on geometrically modified silica gel with hydrated surface; б) shows chromatograms of these three individual vapors on silica gel modified with trimethyl silyl groups; and в) chromatograms of the mixture on silica gel modified with carbon black at different temperatures. The succession of peaks was, however, the inverse compared with silica gel with hydrated surface. The acetone peak had a pronounced tail due to reaction between carbonyl groups and accessible hydroxyl groups of the silica gel carrier. The form of benzene- and n-hexane peaks corresponds to the form of curves illustrating the adsorption heats as functions of the form of adsorption isotherms. The peaks become narrower at higher temperatures. According to theory, the

Graphitized carbon black...

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B110/B101

ratio between band width and retardation time is conserved. A study of chromatograms of individual benzene and hexane vapors at five temperatures allowed estimating their adsorption heats on carbon black from the dependence of logarithm of retardation time versus inverse temperature; results were consistent with calorimetric data. The combination described is well suited for gas chromatography as well as for a rapid physico-chemical analysis of the utilized powders alike. Silica gels modified in this way can also serve as carriers of steady liquid phases. There are 1 figure and 6 references: 3 Soviet-bloc and 3 non-Soviet-bloc. The two references to English-language publications read as follows: Ref. 3: J. Bohemen, Stanley H. Langer, R. H. Perett, J. H. Purnell, J. Chem. Soc., 2444, 1960. Ref. 5: F. T. Eggertsen, H. S. Knight, S. Groennings, Analyt. Chem., 28, 303, 1956.

ASSOCIATION: Laboratoriya adsorptsii i gazovoy khromatografii khimicheskogo fakul'teta Moskovskogo gosudarstvennogo universiteta im. M. V. Lomonosova (Laboratory for Adsorption and Gas Chromatography of the Chemistry Division of Moscow State University imeni M. V. Lomonosov)

Card 3/6

KISELEV, A.V.; MUTTIK, G.G.

Isothermal calorimeter with constant heat exchange. Zhur. fiz.khim. 35 no.9:2153-2155 '61. (MIRA 14:10)

1. Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonosova, khimicheskiy fakul'tet.

(Calorimeters)

S/020/61/136/002/025/034
B004/B056

AUTHORS: Babkin, I.Yu., Kiselev, A.V., and Korolev, A.Ya.

TITLE: Adsorption Heats and Entropies of Hexane and Benzene Vapors on an Aerosils With a Surface Modified by Trimethylsilyl Groups

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol.136, No.2, pp.373 - 376

TEXT: The authors studied the adsorption of hydrocarbon vapors on the surface of aerosils, which had been treated with trimethylchlorosilane. A theoretical calculation of the adsorption energy of n-hexane and benzene molecules (Ref. 3) resulted, with increasing modification of the silicon dioxide, in a drop of the adsoption energy below the value of condensation heat. It was assumed that in the case of sufficiently modified aerosil, the adsorption heat of these hydrocarbons must become negative. It was the purpose of the present work to check this assumption. In order to give the aerosil surface greater homogeneity and reactivity with respect to trimethylchlorosilane, a hydrothermal treatment in an autoclave was carried

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Adsorption Heats and Entropies of Hexane and Benzene Vapors on an Aerosils With a Surface Modified by Trimethylsilyl Groups

S/020/61/136/002/025/034
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out at 120 - 265°C for 8 - 19.5 hours. Specimens of aerosils were obtained, whose surface was occupied by Si $(CH_3)_3$ groups degree of occupation: 0, 60, 85, 90, or 100%. For these specimens, Fig. 1 shows the calorimetric differential adsorption heat Q_a (kcal/mole) as a function of adsorption α (μ-mole/m^2), and Fig. 2 shows the isothermal lines for α as a function of the relative vapor pressure p/p_s. The dropping of Q_a below the condensation heat L was observed, and for the completely (100%) modified specimen, the true adsorption heat was found to be: $Q_a - L = -0.5$ with n-hexane; $Q_a - L = 1.0$ with benzene.

Accordingly, adsorption α decreases considerably with a constantly rising modification (Fig. 2). In the case of large p/p_s, the surface is occupied with hydrocarbon molecules to such a small content that capillary condensation may occur in between. The adsorption heats measured thus include the heat of capillary condensation, and the true adsorption heats must be still lower. From the adsorption isothermal lines and the adsorption heats, the differential adsorption entropies for n-hexane and benzene

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